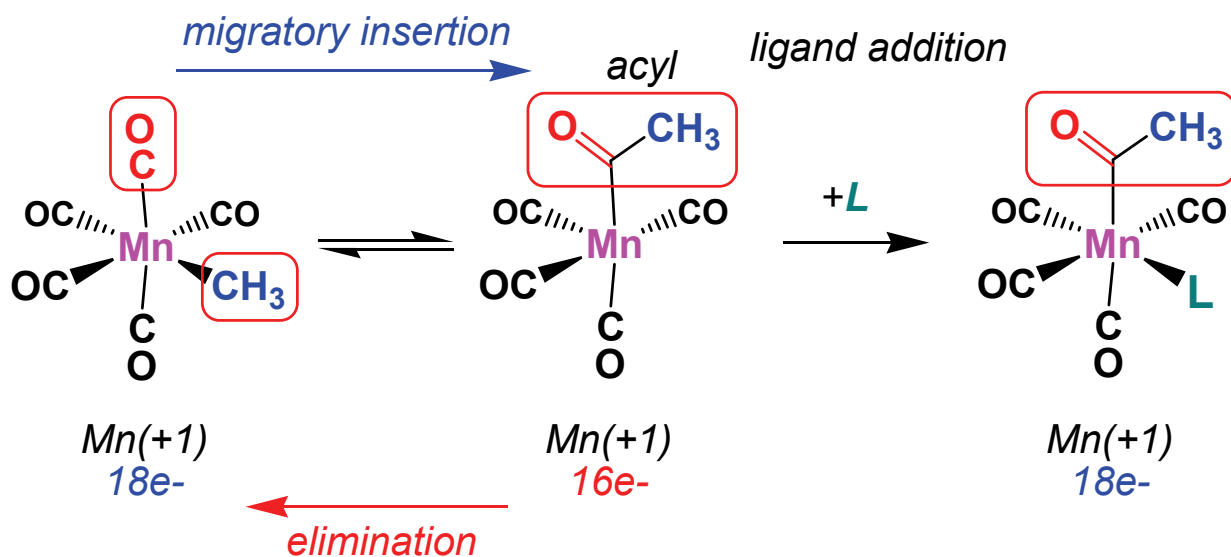


Migratory Insertion

A *migratory insertion* reaction is when a **cisoidal anionic and neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another.

General Features:

- 1) No change in formal oxidation state (exception: alkylidenes)
- 2) The two groups that react must be **cisoidal** to one another
- 3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., β -hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.
- 4) Migratory insertions are usually favored on more electron-deficient metal centers.



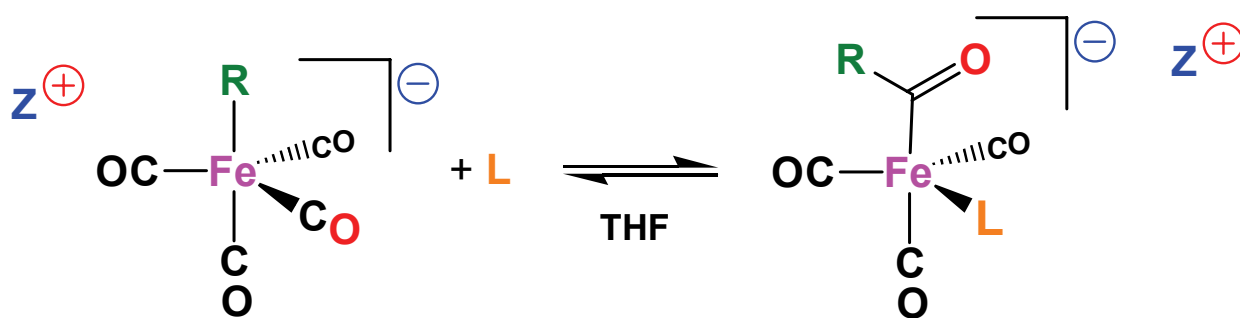
The following are common **anionic** and **neutral** ligands that can do *migratory insertion* reactions with one another:

Anionic: H⁻, R⁻ (alkyl), Ar⁻ (aryl), acyl⁻, O²⁻ (oxo)

Neutral: CO, alkenes, alkynes, carbenes

CO and alkyl migratory insertions (as shown above) are extremely important and are often generically referred to as **carbonylation** reactions. Hydride and CO migratory insertions to produce formyl groups are not common due to the thermodynamic instability of the formyl-metal interaction.

Some Electronic effects



best Lewis acid - can coordinate to electron-rich CO ligands and drain off some e- density



strongest coordinating ligand - best trapping ligand



most electron-rich alkyl group makes the best nucleophile for migrating to the electron-deficient CO

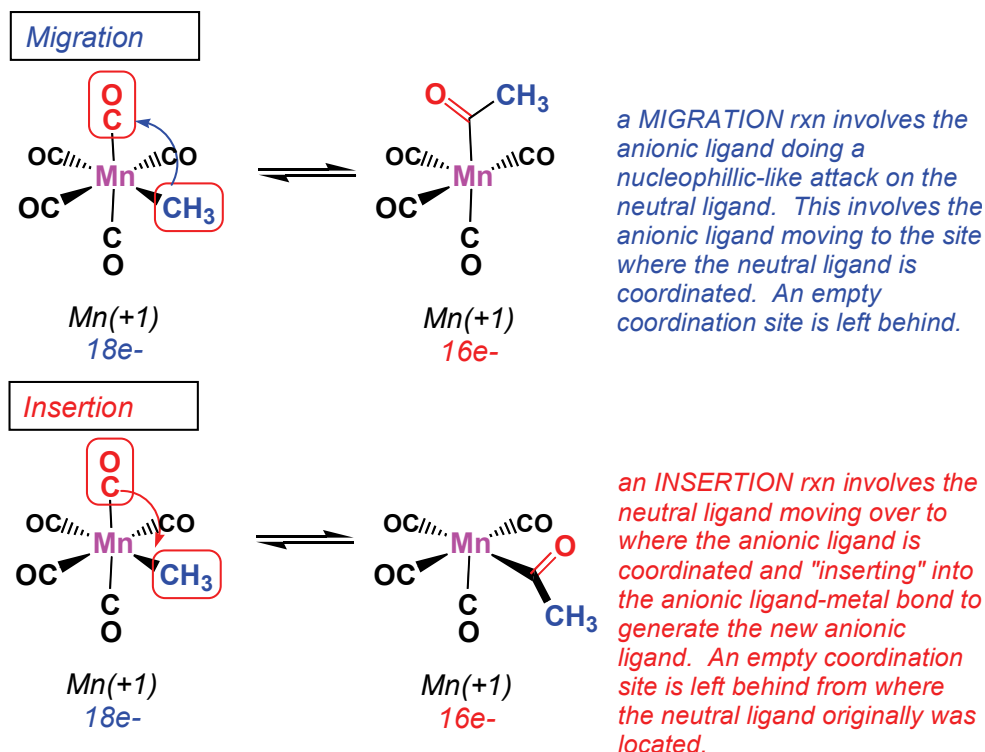


Note that the acyl ligand formed is not as good a donor compared to the starting alkyl. But the metal has gained (replaced) an electron withdrawing CO ligand with a better donating phosphine. Thus, the overall reaction with a trapping ligand is usually towards the migratory insertion.

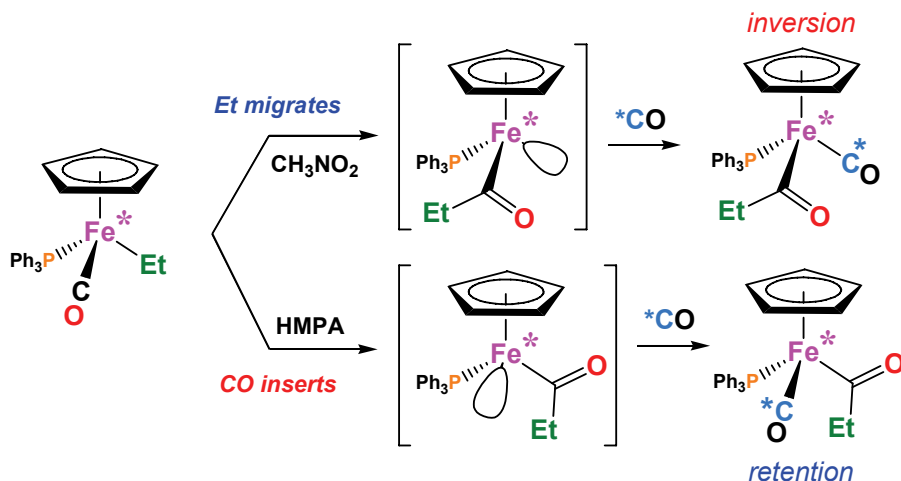
The reason that more electron-deficient metals favor CO-alkyl migratory insertions is that makes the carbon atom of the CO more electrophilic and susceptible to nucleophilic attack from the more electron-rich alkyl group.

Migration vs. Insertion

There are two different “directions” that a migratory insertion can occur. A migration is when the anionic ligand moves and performs a nucleophilic-like intramolecular attack on the electrophilic neutral ligand. An insertion is when the neutral ligand moves and “inserts” into the bond between the metal and anionic ligand. Both of these pathways are illustrated below:



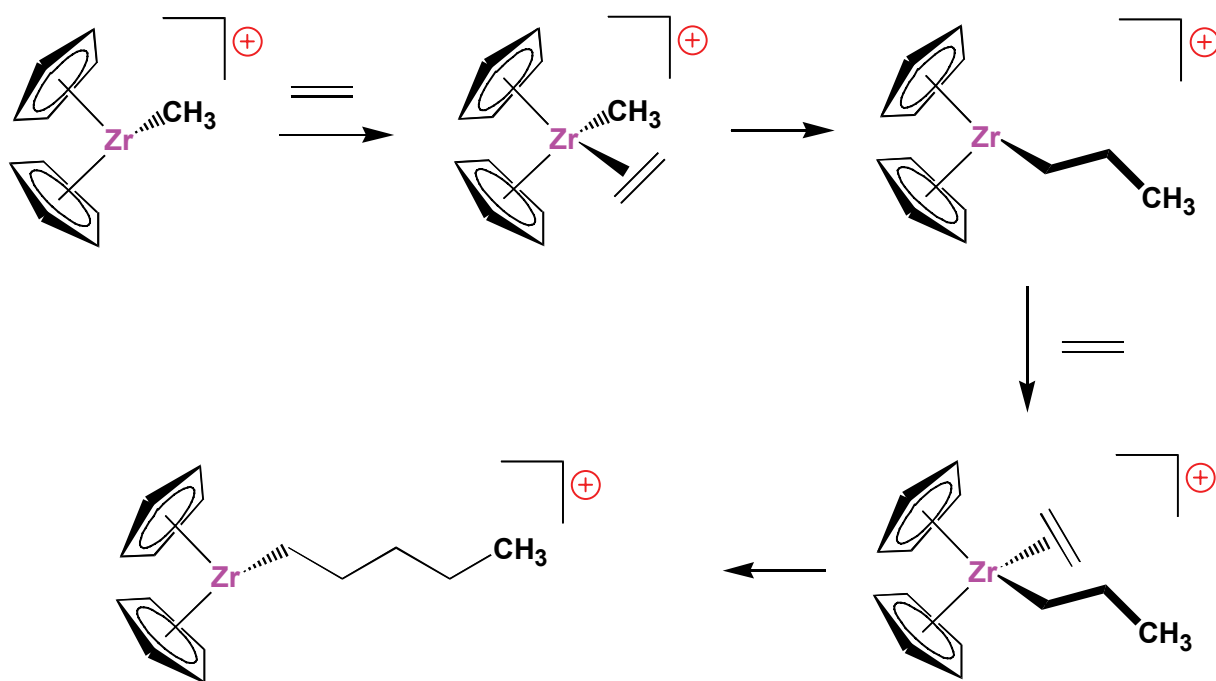
While most systems studied have been shown to do migrations, both are possible. The following example shows a system where both are very similar in energy and the solvent used favors one or the other.



We generally do NOT worry about the exact pathway, that is why we use the redundant term “*migratory insertion*” to indicate that either directional pathway is fine and we don’t know (or care) exactly how the reaction is proceeding. Many organometallic chemists short-cut this and just say *insertion* reaction. They do not usually mean that they know what the mechanism is.

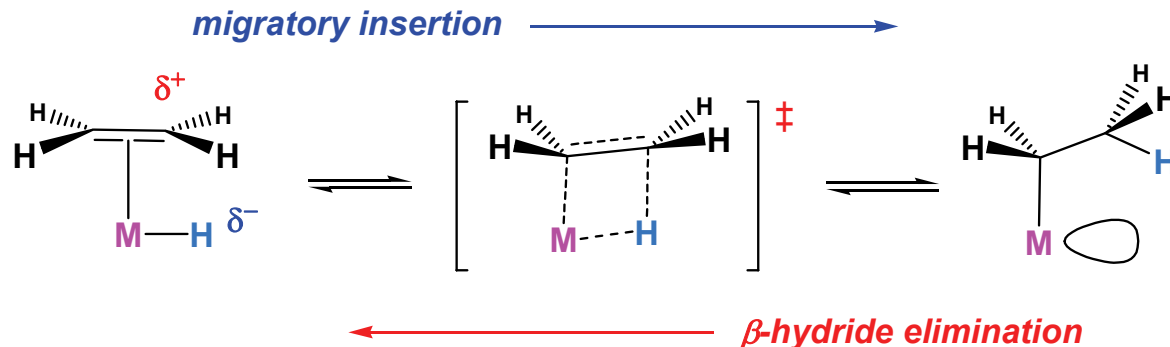
Alkene Migratory Insertions

Alkene and hydride/alkyl migratory insertions are also extremely important and an example is shown below:



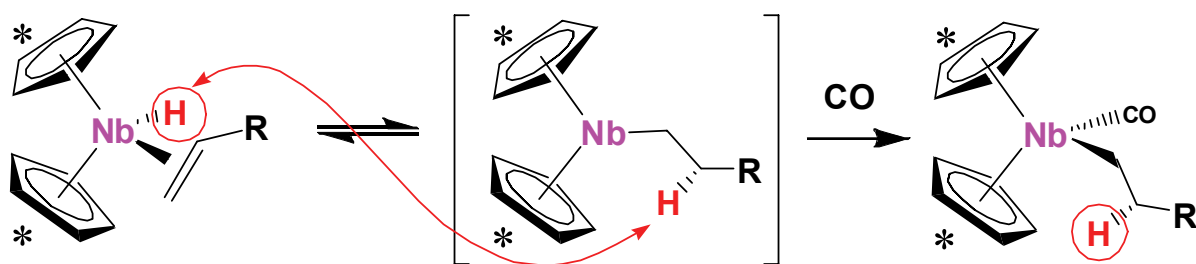
This is the basis for almost all transition metal-based **polymerization** catalysts. A polymerization rxn is just many, many **migratory insertions** of an alkene and alkyl (the growing polymer chain) interspaced with alkene ligand addition reactions.

An alkene and a hydride usually react via a **migration** of the hydride to the coordinated alkene ligand:



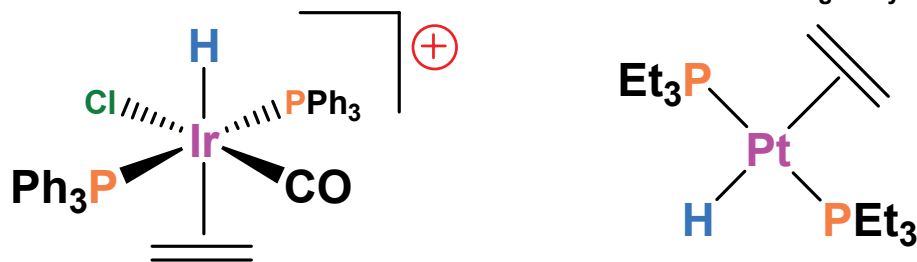
The backwards reaction, of course, is a **β -hydride elimination** and is usually quite favorable if there is an empty orbital cis to the alkyl ligand. Thus, the general importance of having a trapping ligand to coordinate to the empty orbital generated from the migratory insertion.

Bercaw and coworkers demonstrated via spin saturation NMR techniques that the Nb-H-alkene complex shown below was constantly performing a migratory insertion, but that the final product was only observed when a trapping ligand was added to the reaction mixture.

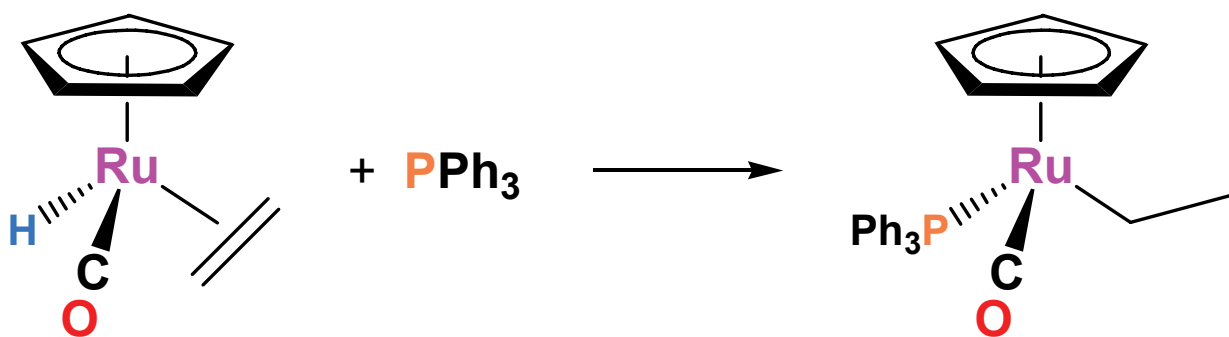


NMR irradiation of the Nb-hydride resonance affects the NMR resonance for the alkyl hydride, demonstrating that they are connected by the migratory insertion mechanism

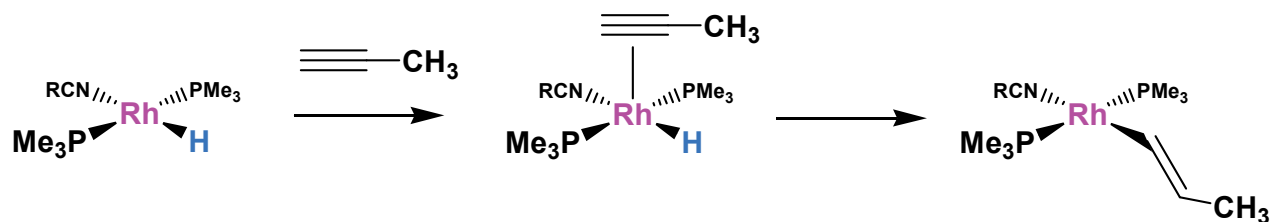
Problem: Why don't either of the complexes shown below do alkene-hydride migratory insertions at room temperature?



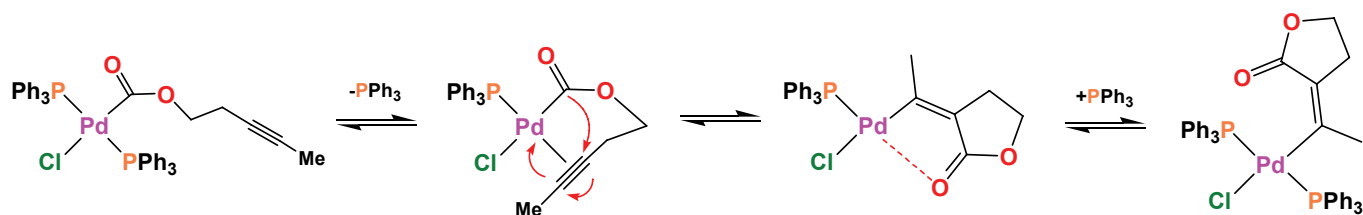
Problem: Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.



Alkynes can also do migratory insertions to produce vinyl groups as shown below:

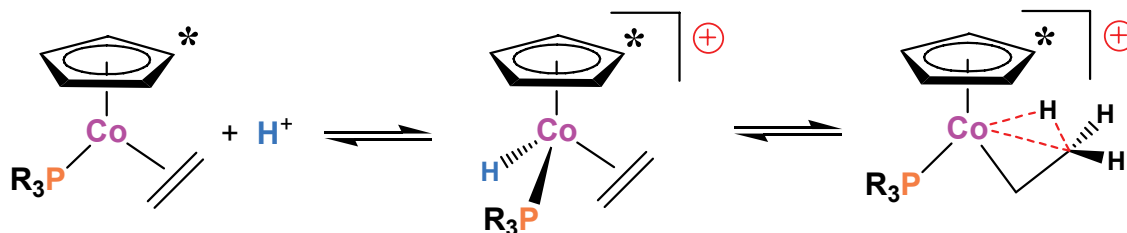


An intramolecular alkyne migratory insertion to make a lactone ring system:



Agostic C-H to Metal Interactions – “Frozen Migratory Insertion”

On occasion one can find an alkene-hydride migratory insertion that doesn't go all the way:



*One of the C-H bonds of the methyl group is within bonding distance to the Co center. This is called an **Agostic** C-H bond interaction.*

Normally this is a transition state structure for a **hydride-alkene migratory insertion** or a **β -hydride elimination**. In some cases, however, it can be observed as a ground-state stable structure.

Because the C-H bond is sharing some of its σ -bond electron density with the metal, the C-H bond is *weakened*. This produces some relatively clear-cut spectroscopic characteristics:

- 1) $\nu_{\text{C-H}}$ infrared stretching frequency is lowered to the mid-2500 cm^{-1} region from a normal value of 2900-3000 cm^{-1}
- 2) the $J_{\text{C-H}}$ coupling constant in the ^{13}C NMR is lowered to around 70-90 Hz from a normal value of 150 Hz.
- 3) the ^1H chemical shift of the agostic proton is in the -10 to -15 ppm region, much like a metal-hydride resonance.

Also note that since the agostic C-H bond is in between a migratory insertion and a β -hydride elimination, small changes in steric or electronic factors on the metal can push it one way or the other. Also since the agostic C-H bond to metal interaction is usually fairly weak, the addition of a better ligand can displace usually in the direction of the M-alkyl complex.

Carbene Migratory Insertions

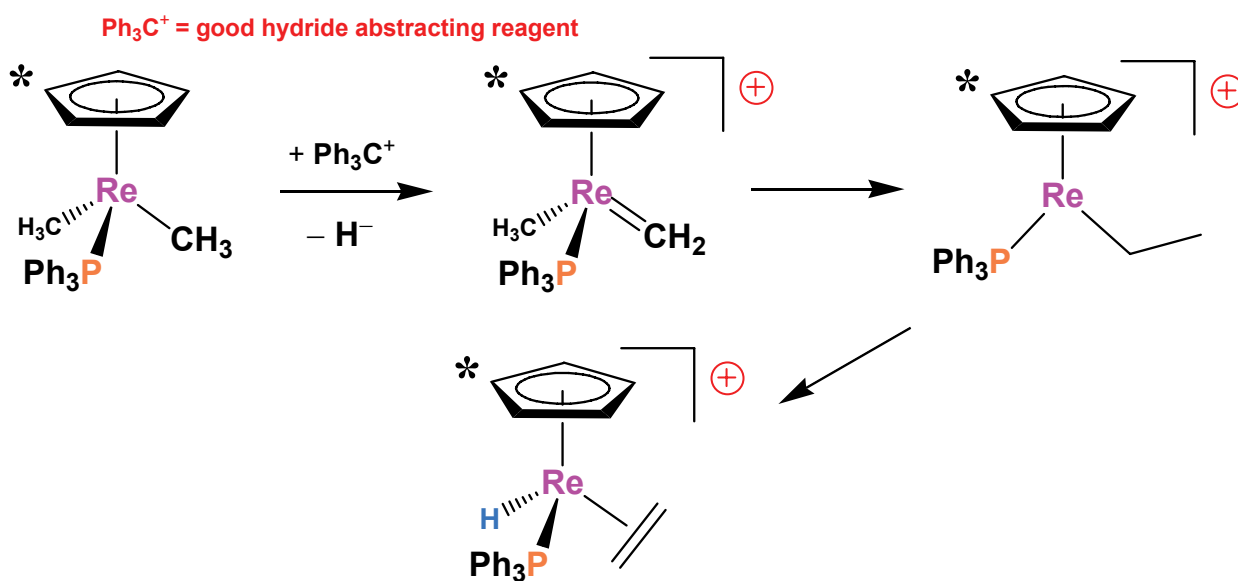
Carbene (or alkylidene) ligands can also do migratory insertions with adjacent anionic ligands:

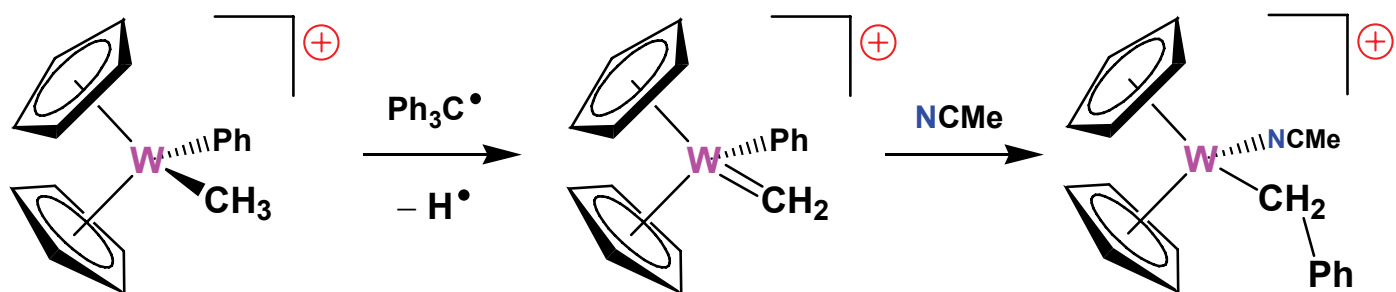


Note that we have somewhat of an electron-counting problem here. Normally a migratory insertion refers to a **neutral ligand** reacting with an **anionic ligand** to produce a **new anionic ligand**. But if we electron-count the carbene as a **dianionic** ligand, we are reacting a monoanionic ligand (**X**) with a dianionic ligand (carbene) to make a new monoanionic ligand. This changes the oxidation state of the metal center and is now formally what we would call a **reductive coupling reaction** (since the metal is being reduced and we are coupling together two ligands).

What most people do is to consider the carbene (or alkylidene) as being a **neutral ligand**. That resolves the electron-counting “problem.”

Note also that in the case of **X = H⁻**, the reverse reaction is called an **α-hydride abstraction or elimination**.

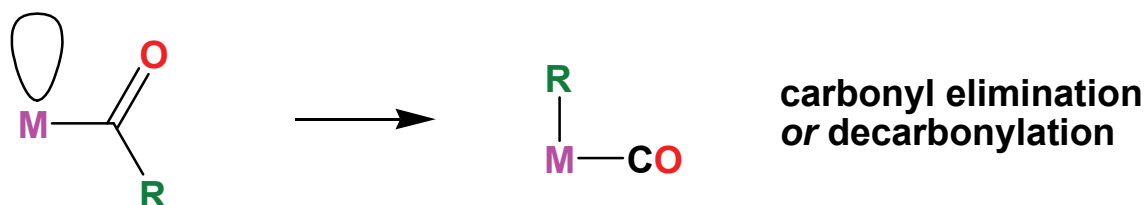
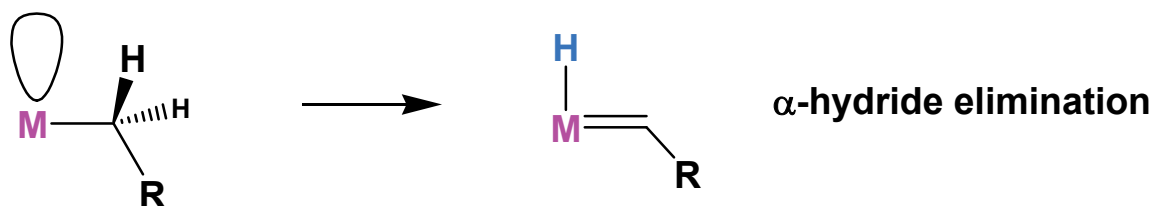
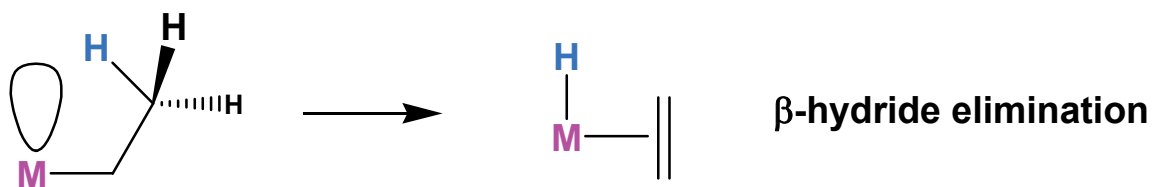




Note that these are reactive “carbenes” and not heteroatom stabilized. They are also probably more Schrock-like, but somewhat electrophillic (note the presence of positive charge on both examples). Fischer carbenes with heteroatoms would probably not be reactive enough for these types of migratory insertion reactions.

Eliminations

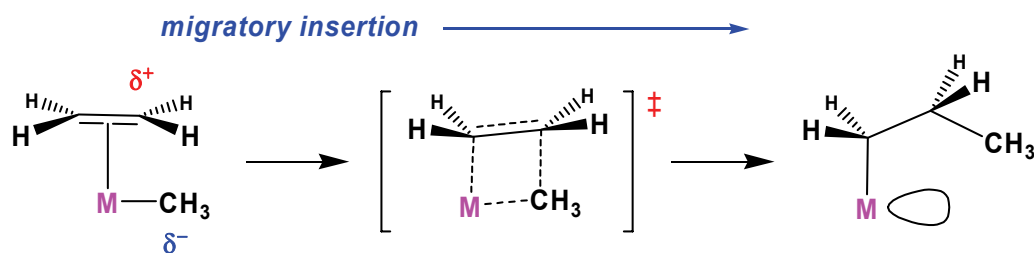
Elimination reactions are just the reverse of migratory insertion reactions. The various common elimination reactions are as follows:



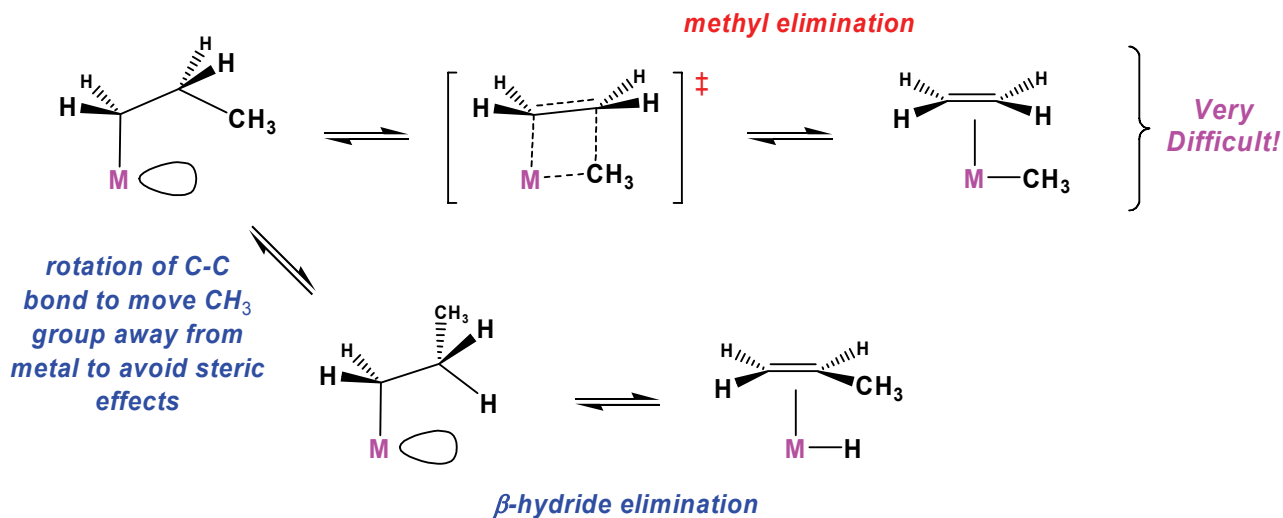
The key points to remember are:

- 1) No change in formal oxidation state (exception: alkylidenes)
- 2) You must have an empty orbital that is **cisoidal** to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.

One of the hardest elimination reactions is the breaking of a C-C bond. For example the following **migratory insertion** is quite common and plays a critical role in polymerization catalysis:

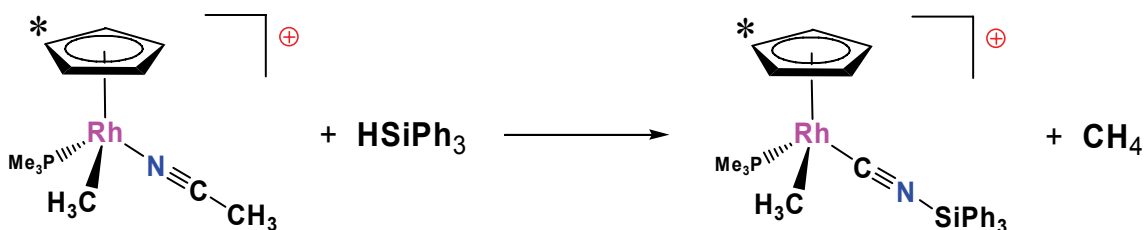


But the reverse **methyl elimination** rxn is very difficult:

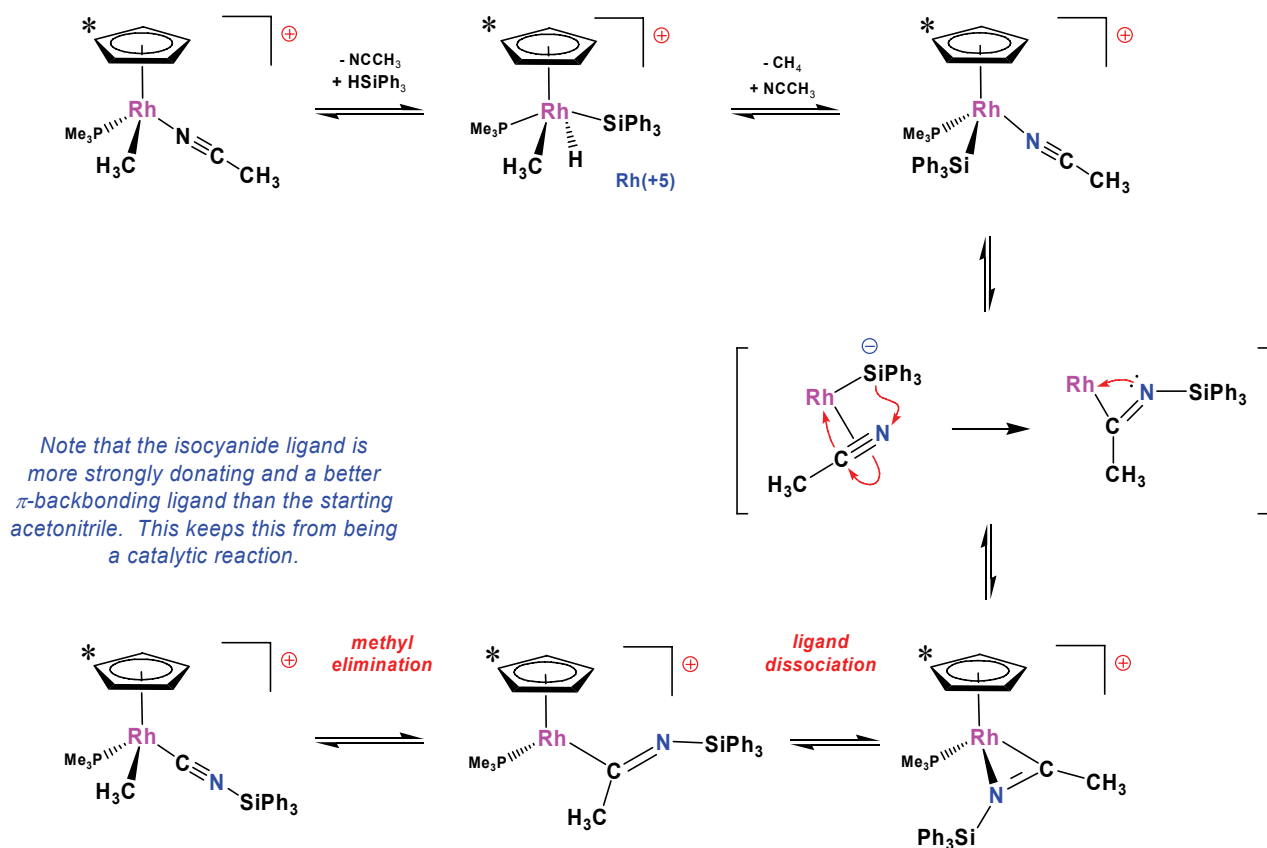


One reason for this is that the C-C σ -bond is surrounded by more reactive C-H bonds that short-circuit the attack on the C-C bond and can instead give a β -hydride elimination. The directed nature of the sp^3 hybridized C-C σ -bond also makes overlap with the empty metal orbital quite difficult.

One unusual example of what is believed to be a methyl elimination reaction is involved in the following transformation (Bergman, *JACS*, 2002, 124, 4192-4193):

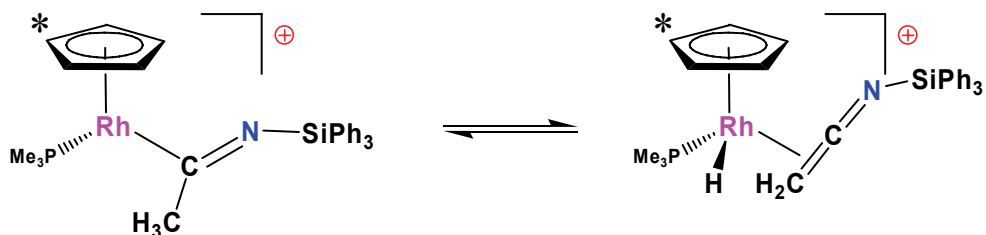


The proposed mechanism for this reaction is shown below:

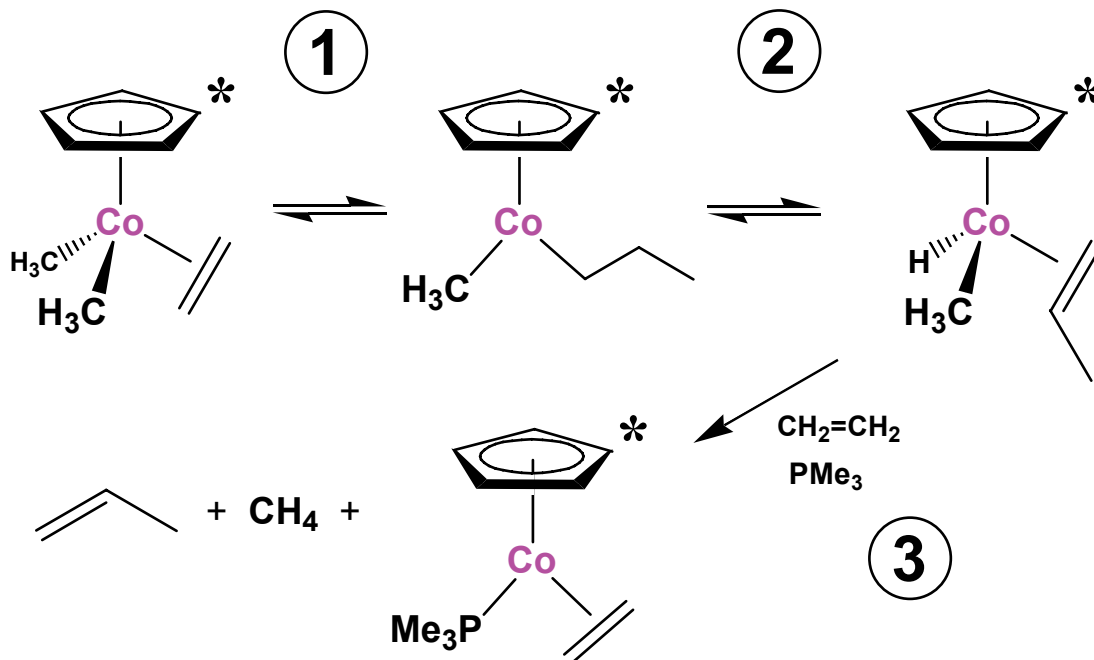


Note that the isocyanide ligand is more strongly donating and a better π -backbonding ligand than the starting acetonitrile. This keeps this from being a catalytic reaction.

One reason that the methyl elimination reaction occurs here is that the β -hydride elimination reaction generates a high energy ketene-imine:



Problem: Identify each step in the following mechanism. Some steps may have several things occurring.



Problem: Sketch out a detailed mechanism and label each step for the following overall reaction.

